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(71) Applicant (*for all designated States except US*): **FACULTES UNIVERSITAIRES NOTRE-DAME DE LA PAIX** [BE/BE]; Rue de Bruxelles 61, B-5000 NAMUR (BE).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **NAGY, Janos, B.** [BE/BE]; Avenue du Bois Carré 5, B-5100 JAMBES (BE). **PIRLOT, Christophe** [BE/BE]; Rue du Brûly, 57, B-5660 PETITE-CHAPELLE (BE). **FONSECA, Antonio** [BE/BE]; Rue Charles de Loupoigne, 15, B-1348 LOUVAIN-LA-NEUVE (BE). **PHILIPPIN, Gregory** [BE/BE]; Rue de la Hêtraie, 7, B-6831 NOIRE-FONTAINE (BE). **DELHALLE, Joseph** [BE/BE]; Rue des Combattants, 19, B-5380 NOVILLE-LES-BOIS (BE). **MEKHALIF, Zineb** [DZ/BE]; Rue Félix Wodon, 29/3, B-5000 NAMUR (BE). **SPORKEN, Robert** [BE/BE]; Place Notre-Dame de la paix, 2 Bte 32, B-5101 ERPENT (BE). **DUBOIS, Philippe** [BE/BE]; Rue Grande,

1, B-4260 CIPLET (BRAIVES) (BE). **ALEXANDRE, Michaël** [BE/BE]; Rue de la Jacinthe, 10, B-4102 OUGREE (BE). **BEYER, Günter** [DE/BE]; Auenweg, 14, B-4700 EUPEN (BE).

(74) Agents: **VAN MALDEREN, Joëlle** et al.; OFFICE VAN MALDEREN, Place Reine Fabiola 6/1, B-1083 BRUSSELS (BE).

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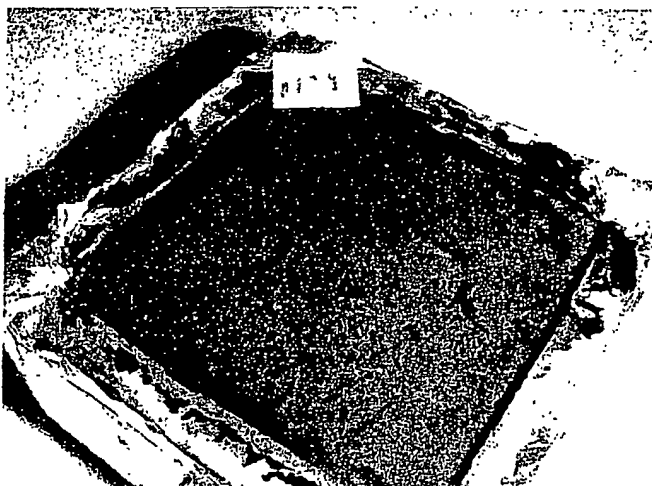
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(54) Title: **NANOCOMPOSITES: PRODUCTS, PROCESS FOR OBTAINING THEM AND USES THEREOF**



(57) Abstract: The present invention is related to nanocomposites comprising polymers, carbon nanotubes and layered silicate nanoparticles. The present invention also concerns methods for obtaining said nanocomposites as well as their uses.

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NANOCOMPOSITES:PRODUCTS, PROCESS FOR OBTAINING THEM, AND USES THEREOF

10

Field of the invention

[0001] The present invention is related to the field of composite materials comprising polymers and carbon nanotubes.

15

State of the art

[0002] Carbon nanotubes were first observed by Iijima in 1991 (S. Iijima, Nature 354 (1991) 56-58). The tubes are built up of carbon atoms arranged in hexagons and  
20 pentagons, with the pentagons concentrated in areas such as the tube ends. Typically, the carbon nanotubes consist of single-wall tubes (hereafter SWNTs) and multi-wall tubes (hereafter MWNTs).

[0003] Carbon nanotubes are flexible and resistant  
25 to the applied stress. They have potential industrial applications in various fields such as in field emission devices, electrical and thermal conductivity, hydrogen storage and molecular sieves.

[0004] Carbon nanotubes can be produced for example,  
30 by arc discharge, by laser ablation or by catalytic decomposition of hydrocarbons.

[0005] The production of some polymer based composite materials comprising carbon nanotubes is described in the literature (C. Pirlet et al., Adv. Eng.

Mater. 4, N° 3 (2002) 109-114; B. McCarthy et al., *J. Phys. Chem. B* 106 (2002) 2210-2216; V. K. Gupta et al., *World Patent Information* 22 (2000) 185-189). Nevertheless, industrials find major difficulties to get the homogeneous  
5 dispersion of the nanotubes in the polymer matrices, resulting in the transfer of only parts of the interesting properties from the carbon nanotubes to the composite materials.

#### 10 Aims of the invention

[0006] The present invention aims to provide nanocomposites comprising polymers and carbon nanotubes , which would not present the drawbacks of the nanocomposites of the state of the art.

15 [0007] More precisely, the present invention aims to provide nanocomposites with enhanced physical properties, namely enhanced mechanical and electrical properties, comparatively to the composites of the state of the art, which could be industrially interesting.

20 [0008] Another object of the present invention is to provide nanocomposites which could be produced industrially with relative ease and relative moderate cost.

#### Summary of the invention

25 [0009] The present invention is related to nanocomposite, comprising as components polymers, carbon nanotubes and layered silicate nanoparticles.

[0010] Preferably, said nanocomposite components are homogeneously dispersed.

30 [0011] Preferably, polymers are selected from the group consisting of thermoplastic polymers, polyolefins, vinylic polymers, acryl-nitrile polymers, polyacrylates, elastomers, fluoro-polymers, thermoplastic polycondensates, duroplastic polycondensates, silicon resins, thermoplastic

elastomers, co- and ter-polymers, grafted polymers and mixtures thereof.

[0012] Preferably, the carbon nanotubes are selected from the group consisting of SWNTs, and MWNTs, said carbon  
5 nanotubes being pure, partly purified, crude or functionalized.

[0013] Preferably, the layered silicate nanoparticles are organomodified layered silicate nanoparticles.

10 [0014] Preferably, the layered silicate nanoparticles are intercalated organo-modified layered silicates from the chemical class of 2:1 phyllosilicate and smectite.

[0015] Advantageously, the total content of the  
15 layered silicates and carbon nanotubes varies from 0.01 to 50 wt.%, preferably from 0.5 to 25 wt%, and most preferably between 1 and 10 wt.%.

[0016] Advantageously, the carbon nanotubes to the layered silicate nanoparticles weight ratio varies from  
20 0.01 to 100, and preferably between 0.1 and 10.

[0017] Preferably, the nanocomposite of the present invention further comprises at least one microfiller, preferably in a quantity varying from 1 to 70 wt%.

[0018] The present invention is also related to the  
25 use of said nanocomposites.

[0019] In particular the present invention is related to different uses of the nanocomposites according to the present invention:

- in anti-fire protection structures
- 30 ▪ as flame retardant
- as light-emitter
- as anti-static materials
- as conductive wires

- as wire protector sheath
  - as anti-cracks in surface protection coatings
  - as anti-cracks in reinforced materials
  - as surface protection coatings
- 5   ▪ as reinforced materials.

[0020]           Another object of the present concerns the use of the nanocomposites of the invention as flame retardant.

[0021]           The present invention is also related to a  
10   process for obtaining the nanocomposite of the invention, said process comprising the step of providing the different components i.e. the polymers, the carbon nanotubes, the layered silicate nanoparticles, and if necessary the microfiller, and the step of mixing said different  
15   components in adequate conditions so as to obtain an homogenous dispersion.

[0022]           Preferably, in said process, the step of providing the carbon nanotubes comprises the step of producing said carbon nanotubes on a M/MgO catalyst,  
20   wherein M is selected from the group consisting of Co, Fe, Ni, Mo or their mixtures, and M represents 0.1-50 wt% of the catalyst, the MgO being prepared in situ from metallic magnesium.

[0023]           Preferably, in said process, the step of  
25   providing the carbon nanotubes further comprises the step of purifying the crude carbon nanotubes as produced in claim 14, by oxidation of the crude nanotubes at 250-500 °C in pure or diluted oxygen for a given time, prior to the dissolution of the spent catalyst, while the nanotubes are  
30   well dispersed on it.

[0024]           In one preferred embodiment of said process, the step of providing the carbon nanotubes further comprises the step of drying the carbon nanotubes produced

to obtain a very fine powder, by lyophilisation of a nanotubes/water "wet cake" containing preferably 80-95 wt% of water.

[0025] In another preferred embodiment of said process, the step of providing the carbon nanotubes further comprises the step of drying the carbon nanotubes produced to obtain a very fine powder, by azeotrope distillation of a nanotubes/water "wet cake" containing preferably 80-95 wt% of water and wherein benzene, toluene or xylene is used to make the azeotrope.

#### Definitions

[0026] It should be noted that in the present description the wordings "nanocomposites based on ..." and "nanocomposites comprising" are equivalent.

[0027] The terms "filler" and "microfiller" refer to any other constituent of the nanocomposite except the polymer.

[0028] It is meant by "dispersion" the dispersion of the components, namely the carbon nanotubes, in the polymer matrix.

#### Short description of the drawings

[0029] Figures 1a and 1b give images of the residues, after cone calorimeter analysis at 35 kW/m<sup>2</sup>, of nanocomposites comprising EVA (EVA = ethylene-vinyl acetate copolymer; Escorene UL 00328) as polymer, and 4.8 wt.% of purified MWNTs (Fig. 1a: sample 2) or organo-clay (Fig. 1b: sample 6). A cone calorimeter analysis of residues of EVA-based nanocomposites containing both 2.4 wt.% of purified MWNTs and 2.4 wt.% of organo-clay is also represented on Fig. 1c: sample 7.

Detailed description of the inventionI. Description of the starting materialsI.A.- Polymers

5 [0030] The polymers that can be used can be selected from thermoplastic polymers (like polystyrene, etc.), polyolefins (like polyethylene, polypropylene, etc.), vinylic polymers (like PVC or PVDF), acryl-nitrile polymers, polyacrylates, elastomers, fluoro polymers, 10 thermoplastic polycondensates (like PA, PC, PETP), duroplastic polycondensates, silicon resins, thermoplastic elastomers, co-polymers (like EVA, etc.), ter-polymers, grafted polymers and also their blends.

[0031] A summary of suitable polymers can be found 15 at: Hans Dominghaus "Die Kunststoffe und ihre Eigenschaften" 2 Auflage, VDI-Verlag, Seite VII bis XI.

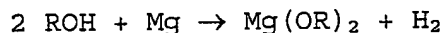
I.B.- Nanotubes

[0032] The nanotubes are SWNTs, MWNTs or their 20 mixtures. The nanotubes are either pure, partly purified, crude or functionalized. The crude nanotubes contain the spent catalysts and the other forms of carbon that are by-products of the nanotubes synthesis. The by-products are amorphous carbon, pyrolytic carbon, carbon nanoparticles, 25 carbon onions, fullerenes, metal nanoparticles encapsulated in carbon, carbon fibres. The partly purified nanotubes contain the by-products that could not be eliminated during the purification. The spent catalysts are oxides, mixed oxides, aluminosilicates, zeolites, oxycarbides, mixed 30 oxycarbides, carbonates, metal hydroxides, metal nanoparticles, etc.

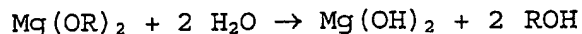
[0033] Crude and purified nanotubes samples were used to prepare the nanocomposites. Crude MWNTs were produced by catalytic decomposition of acetylene on



Co-Fe/Al(OH)<sub>3</sub> catalyst at 700 °C and the crude SWNTs were produced by catalytic decomposition of methane at 950 °C on either Co/MgO catalyst or M/MgO\* catalyst (M = Co, Fe, Ni, Mo or their mixtures; M = 0.1-50 wt% of the catalyst). The  
5 Co/MgO catalyst was prepared by impregnation of commercial MgO by an alcoholic solution of a cobalt salt while the M/MgO\* catalyst was prepared as follows: First, 10 g of metallic magnesium are introduced in 200 ml of alcohol (i.e. MeOH, EtOH, ...) contained in a 1 liter flask equipped  
10 with a reflux condenser and a mechanical stirrer. After about five minutes the alcohol begins to react with magnesium as follows :

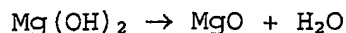


15 [0034] The speed of the reaction is controlled by cooling down the flask if the alcohol is boiling too much. Secondly, the metal salt (e.g. 13.727 g of Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) is dissolved in 50 ml of alcohol by sonication and then added to the magnesium alkoxide solution under vigorous stirring.  
20 The solution gellifies rapidly but the stirring is prolonged to homogenise the gel. Afterwards, 300 ml of water are added to the gel under stirring to form a broken white gel as follows :



25 [0035] The total amount of alcohol (250 ml) is distilled out by azeotropic distillation, with refilling 50 ml of water every 50 ml of distillate to keep the volume of gel constant. Finally the gel is allowed to stand overnight at room temperature for maturation and it is dried either  
30 under supercritical conditions or by lyophilisation, preferably. The dried residue is further dehydrated by heating under an air flow, from room temperature to 370 °C at 3 °C/min, kept at 370 °C for 2 hours and cooled down to

room temperature at 6 °C/min. The latter dehydration proceeds as follows :



[0036] The dehydrated powder collected is called  
5 M/MgO\* catalyst and it was found to be very active for the production of SWNTs by catalytic decomposition of methane in the presence of hydrogen.

[0037] Purified MWNTs were obtained after dissolution of the support in boiling concentrated sodium  
10 hydroxide and dissolution of the catalyst in concentrated hydrochloric acid.

[0038] Purified SWNTs were obtained after dissolution of the catalyst and support in concentrated hydrochloric acid, followed by filtration and washing until  
15 pH = 5-7 to obtain a nanotubes/water "wet cake", containing ca. 80-95 wt.% of water, that is dried at 120°C overnight. In order to decrease the metal content of the purified SWNTs, it was found that oxidation of the crude SWNTs at 250-500 °C in air for a given time (preferably one hour at  
20 300 °C), prior to the dissolution of the catalyst and support, was very effective because the nanotubes are well dispersed on the spent catalyst. For better dispersion of the purified SWNTs in the polymer matrix, it was also found that the lyophilisation of the nanotubes/water "wet cake"  
25 was more convenient than its drying at 120° overnight. In fact, the drying at 120 °C provides very hard "rocks" of SWNTs, while the lyophilised SWNTs is a very fine powder.

[0039] The catalyst and support content of the nanotubes samples are shown in Table 1.

Table 1: Characteristics of the nanotubes samples and their catalyst and support content.

Sample <sup>(a)</sup>	Nanotubes		Catalyst		Support	
	Length ( $\mu\text{m}$ )	Diameter (nm)	Co (wt.%)	Fe (wt.%)	Al <sub>2</sub> O <sub>3</sub> (wt.%)	MgO (wt.%)
Crude MWNTs	ca. 50	5-15	0.3	0.3	19	-
Purified MWNTs	ca. 50	5-15	0.2	0.3	0.2	-
Crude SWNTs-1	ca. 10	1-2	2.5	-	-	92.5
Purified SWNTs-1	ca. 10	1-2	15	-	-	0
Oxidised purified and lyophilised SWNTs-1	Ca. 10	1-2	0.3	-	-	0
Crude SWNTs-2	Ca. 10	1-2	12	-	-	79
Purified SWNTs-2	Ca. 10	1-2	14	-	-	0
Oxidised purified and lyophilised SWNTs-2	Ca. 10	1-2	0.5	-	-	0
Crude SWNTs-3	Ca. 10	1-2	-	12	-	79
Purified SWNTs-3	Ca. 10	1-2	-	15.5	-	0
Oxidised purified and lyophilised SWNTs-3	Ca. 10	1-2	-	0.8	-	0

<sup>(a)</sup> : SWNTs-1 were produced on Co/MgO; SWNTs-2 were produced on Co/MgO\*; SWNTs-3 were produced on Fe/MgO\*.

5

#### I.C.- Layered silicate nanoparticles

[0040] Silicate nanoparticles are intercalated organic-modified layered silicates from the chemical class of 2:1 phyllosilicate or smectite such as montmorillonite, hectorite, saponite, etc.

[0041] Montmorillonite is the most commonly used layered silicate (clay). It is a crystalline 2:1 layered clay mineral with a central alumina octahedral sheet sandwiched between two silica tetrahedral sheets. When

these nanoparticles are dispersed in a polymer, they are either intercalated by 'macromolecules or exfoliated. Therefore, intercalated structures show regularly alternating layered silicates and polymer chains in contrast to exfoliated structures in which the individual clay layers are delaminated and dispersed in the polymer matrix.

[0042] The best performances are commonly observed for the exfoliated nanocomposites. The two extreme situations can however coexist in the same material.

[0043] The polymer-silicate compatibility is promoted by an ion-exchange reaction of the silicate interlayer sodium cations with alkyl ammonium cations or the like, hereafter called organo-clays (G. Beyer, Polymer News, November 2001).

[0044] The investigated organo-clay mineral, Nanofil<sup>®</sup>15 was supplied by Süd-Chemie (Germany). It is a sodium montmorillonite with sodium cations exchanged by distearyldimethylammonium cations. This organo-clay contains about 30 wt.% of the organic cation within its structure and is characterized by an interlayer distance of 2.8 nm.

## II. Preparation of the composite materials containing carbon nanotubes

[0045] The nanocomposites of polymers based on carbon nanotubes and silicate nanoparticles are prepared applying preferably one of the different methods described hereafter. These methods can be divided in two categories that are called "mechanical methods" and "solution methods" depending on the dispersion of the constituents that is achieved mechanically or in solution, respectively.

## II.A.- Mechanical methods

### *Extrusion method:*

- [0046] In that method, extruders are used to mix the molten polymer with the carbon nanotubes and organo-clays.
- 5 The organo-clays are preferably mixed either with the carbon nanotubes or with the polymer before the extrusion.
- [0047] The polymer, carbon nanotubes and organo-clays can also be mixed together or not before the extrusion.
- 10 [0048] The form, length and rotation speed of the extruder screws are adjusted to obtain a suitable mixing time. The efficiency of the mixing depends on the screw parameters (design, relation of length to diameter and rotation speed) but also on the extrusion temperature that
- 15 regulates the viscosity of the polymer. The temperature is either uniform or varies along the screw depending on the desired nanocomposite.

### *Reactive extrusion method:*

- 20 [0049] The extrusion parameters are the same as for the "extrusion method" except that an additional chemical reaction (like cross-linking, etc.) takes place during the extrusion step.

### *Batch method:*

- [0050] In that method, the molten polymer is mixed with the carbon nanotubes and organo-clays in a reactor (internal mixer or rolling mill) at a given temperature or for a temperature cycle. The nanocomposite components are
- 30 introduced either together or one by one. A chemical reaction can also take place between the components.

[0051] The samples 1-12b of Table 2 were prepared using the internal mixer type Brabender with a mixing chamber of 72 ml equipped with roller blades. Rotation

speeds of 45 or 120 rpm were used (Table 2). The mixing time was 10 minutes and mixing temperatures of 130 or 140 °C were used (Table 2). In the preferred embodiment, the polymer EVA (50 g) is introduced in the mixing chamber  
5 preheated at 125 °C and, when the polymer is molten, the filler is added and the mixing is prolonged for 10 minutes. Afterwards, the chamber is opened and the nanocomposite is recovered.

## 10 II.B.- Solution methods

### *Solution method a:*

[0052] In that method, the nanocomposite constituents are dispersed in the solvent at the appropriate temperature by stirring. The dispersion depends  
15 on the order of mixing of the various nanocomposite constituents. The stirring is produced mechanically or by sonication. Afterwards, the solvent is eliminated either by filtration or by evaporation at the appropriate temperature. They can also be dispersed in solvents, either  
20 individually or not, prior to their mixing.

[0053] The preferred solvents are solvents characterized with solubility parameters close to the solubility parameter of the investigated polymer matrix. Mixtures of solvents are also effective.

25 [0054] Surfactants such as the ones known in the field can also be added to the nanocomposite constituents to enhance the dispersion. Non solvents (thus with solubility parameters far from solubility parameter of the investigated polymer matrix) can also be added to the  
30 nanocomposite constituents dispersion prior to its filtration.

*Solution method b:*

[0055] In that method, the carbon nanotubes and the polymer are dispersed in the solvent at the appropriate temperature by stirring like in the "solution method a".  
5 Afterwards, the solvent is eliminated either by filtration or by evaporation at the appropriate temperature. The organo-clay and additional nanocomposite constituents are introduced applying one of the "mechanical methods".

10 *Solution method c:*

[0056] In that method, the organo-clay and the polymer are dispersed in the solvent at the appropriate temperature by stirring like in the "solution method a". Afterwards, the solvent is eliminated either by filtration  
15 or by evaporation at the appropriate temperature. The carbon nanotubes and additional nanocomposite constituents are introduced applying one of the "mechanical methods".

*Solution method d:*

20 [0057] In that method the polymer is replaced by its precursors. Then, the nanocomposite constituents are dispersed in the solvent at the appropriate temperature by stirring like in the "solution method a". Afterwards, after reaching good dispersion of the nanocomposite constituents,  
25 the polymerisation is performed. The solvent is eliminated either by filtration or by evaporation at the appropriate temperature.

*Solution method e:*

30 [0058] In that method, the carbon nanotubes are dispersed in the solvent at the appropriate temperature by stirring like in the "solution method a" but, the polymer is replaced by its precursors. Afterwards, after reaching good dispersion, the polymerisation is performed. The

solvent is eliminated either by filtration or by evaporation at the appropriate temperature. The organo-clay and additional nanocomposite constituents are introduced applying one of the "mechanical methods".

5

*Solution method f:*

[0059] In that method, the organo-clay is dispersed in the solvent at the appropriate temperature by stirring like in the "solution method a" but, the polymer is  
10 replaced by its precursors. Afterwards, after reaching good dispersion, the polymerisation is performed. The solvent is eliminated either by filtration or by evaporation at the appropriate temperature. The carbon nanotubes and additional nanocomposite constituents are introduced  
15 applying one of the "mechanical methods".

III. Measure of the properties of the composite materials

III.A- Transmission electron microscope (TEM) analysis

[0060] The dispersion of the nanotubes in the  
20 polymer matrix was studied by transmission electron microscopy (TEM) with Philips Tecnaï T10. For analysis, the composite samples were cut into very thin slices (about 80 nm) by an ultra-microtome. Then, the slices were deposited onto a conventional TEM grid.

25 [0061] All the samples present a relatively homogeneous dispersion of the nanotubes in the polymer matrix (Tables 2 and 3; Decreasing dispersion order: +++ > ++ > + > - > -- > ---). Nevertheless, applying MWNTs, the addition of organo-clay, as well as the use of crude  
30 nanotubes and the increase of the wt.% of the nanotubes lead to a more homogeneous dispersion. Applying SWNTs, the best dispersion was obtained using the "oxidised purified and lyophilised" samples (Table 3). The addition of



organo-clay was also helpful to the dispersion of the SWNTs in the polymer matrix.

### III.B.- TGA analysis

5 [0062] TGA analysis in air at 20 K/min were carried out on the polymer EVA (Escorene UL 00328) and on EVA-based nanocomposites. The results are summarised in Table 2.

[0063] As can be seen in Table 2, the  $T_{\max}$  is higher for the EVA based nanocomposites than for the polymer EVA;  
10  $T_{\max}$  is the maximal temperature of the second and therefore main degradation peak of the EVA degradation under oxidative conditions according to G. Beyer, Polymer News, November 2001.

[0064] From the TGA results in Table 2 concerning  
15 the nanocomposites containing 2.4 wt.% of either purified MWNTs (sample 1) or organo-clay (sample 5), the thermal stabilisation effect in air of the polymer fillers is as follows: organo-clay > purified MWNTs.

[0065] From the TGA results in Table 2 concerning  
20 the nanocomposites containing 4.8 wt.% of either purified MWNTs (sample 2), crude MWNTs (sample 8a), or organo-clay (sample 6), the thermal stabilisation effect in air of the polymer fillers is as follows: crude MWNTs > organo-clay > purified MWNTs.

25 [0066] The increase of the organo-clay content from 2.4 to 4.8 wt.% causes decrease of the  $T_{\max}$  (Table 2).

[0067] As distinct from the effect of increasing the organo-clay content, increasing the content of purified MWNTs causes a small increase of the  $T_{\max}$  (Table 2).

30 [0068] Nevertheless, the maximal thermal stabilisation effect in air was observed when using 5 wt.% of crude MWNTs (sample 8a). Surprisingly, crude MWNTs are much more efficient fillers for thermal stabilisation of polymers than purified MWNTs. This improvement may be

caused by the concomitant presence of MWNTs, catalyst support and catalyst.

[0069] From the TGA analysis of the nanocomposite containing 2.4 wt.% of purified MWNTs and 2.4 wt.% of  
5 organo-clay (sample 7; Table 2), it is evident from the  $T_{\max}$  that there is no synergistic improvement effect in thermal stabilisation caused by the concomitant use of both purified MWNTs and organo-clay as polymer fillers.

### 10 III.C.- Cone calorimeter analysis

[0070] It is reported (G. Beyer, Polymer-News, November 2001) that from an engineering point of view, it is important to know what hazards within a fire must be prevented and only then strategies for measurements and  
15 improvements can be developed.

[0071] Extensive research at NIST (National Institute for Standards and Technology, USA) led to the important conclusion which allows significant simplification of the problem for hazards in fires: The  
20 heat release rate, in particular the peak heat release rate, is the single most important parameter in a fire and can be viewed as the "driving force" of the fire.

[0072] Therefore, today the universal choice of an engineering test for flame retardant polymers is the cone  
25 calorimeter. The measuring principle is the oxygen depletion with a relationship between the mass of oxygen consumed from the air and the amount of heat released.

[0073] The cone calorimeter is standardized as ASTM E 1354 and ISO 5660.

30 [0074] Cone calorimeter analysis using  $35 \text{ kW/m}^2$  were carried out on the polymer EVA (Escorene UL 00328), on polymer PE (BP8063), on EVA based nanocomposites and on PE based nanocomposites. The results are summarised in Tables 2 and 3. In these tables, the following important

parameters were used to characterise the flame retardant effect of the different polymer fillers. These parameters are:

- 5       > *PHRR (Peak of Heat Release Rate)*, which represents the maximum heat release rate during combustion.
- > *Cracks density*, estimated from the residues of the cone calorimeter analysis (decreasing cracks density order: +++ > ++ > + > - > -- > ---).
- 10     > *Surface quality*, estimated from the residues of the cone calorimeter analysis (decreasing surface quality order: +++ > ++ > + > - > -- > ---).

#### **III.C.a.- PHRR results**

[0075]       From the *PHRR* point of view, it is evident  
15 from the results in Table 2 that all of the filled polymers used have improved flame retardant effects.

[0076]       For EVA and EVA based nanocomposites containing 2.4 wt.% of filler, the *PHRR* decreases as follows: EVA > organo-clay ~ purified nanotubes.  
20 Surprisingly the purified nanotubes are as effective in the reduction of *PHRR* as the nanocomposites bases on organo-clay.

[0077]       For EVA and EVA based nanocomposites containing 4.8 wt.% of filler, the *PHRR* decreases as  
25 follows: EVA > organo-clay > purified nanotubes = crude nanotubes.

[0078]       Surprisingly the crude nanotubes are as effective in the reduction of *PHRR* as the purified nanotubes.

30 [0079]       Increasing the filler content from 2.4 to 4.8 wt.% causes an additional flame retardant effect if the filler is organo-clay and it becomes very important when purified or crude MWNTs are used.

[0080] A surprising synergism flame retardant effect between MWNTs and organo-clay was observed for the nanocomposite containing 2.4 wt.% of purified MWNTs and 2.4 wt.% of organo-clay (sample 7). The latter sample was found  
5 to be the best flame retardant nanocomposite.

[0081] From the PHRR point of view, the variation of the screw velocity from 45 rpm (sample 8a) to 120 rpm (sample 8b) caused no flame retardant changes on the nanocomposites containing 4.8 wt.% of crude MWNTs.

10 [0082] For PE and PE based nanocomposites containing 4.8 wt.% of filler (Table 3), the PHRR decreases as follows: purified SWNTs > crude SWNTs > PE > purified MWNTs > crude MWNTs. The same order was found for the nanocomposites containing 9.1 wt.% of filler.

15 [0083] From the PHRR and time to ignition results (Table 3), MWNTs work as flame retardant in PE with no reduction of time to ignition while SWNTs do not work as flame retardant in PE.

20 ***III.C.b.-Cracks density results and surface quality results***

[0084] For the flame retardant EVA based nanocomposites containing 2.4 wt.% of filler (Table 2), the cracks density increases in the order: purified MWNTs < organo-clay. Again, a very important synergistic effect  
25 reducing the cracks density to zero, was surprisingly observed when the nanocomposite contains 2.4 wt.% of purified MWNTs and 2.4 wt.% of organo-clay (Fig. 1c).

[0085] The surprising synergistic effect for improved flame retardancy by the filler combination  
30 nanotube and organo-clay can be explained by the improved closed surface. This improved char acts as an insulating and non-burning material that reduces the emission of volatile products (fuel) into the flame area. The less cracks are present, the better is the reduction of emission

and the reduction of PHRR. The fillers play an active role in the formation of this char but obviously also strengthen it and make it more resistant to mechanically cracking.

[0086] For the flame retardant EVA based  
5 nanocomposites containing 4.8 wt.% of filler (Table 2; Figs 1a-b), the cracks density increases in the order: crude MWNTs < purified MWNTs < organo-clay.

[0087] Increasing the filler content of the EVA based nanocomposites from 2.4 to 4.8 wt.% (Table 2), causes  
10 crack density decreases using purified MWNTs or organo-clay.

[0088] An analogous flame retardant behaviour is observed with crude or purified SWNTs of different types specified in Table 1. Among the nanocomposites including  
15 crude or purified SWNTs, better behaviours are observed with SWNTs-2 and -3. The better behaviours of the SWNTs-2 and -3 may be due to the higher nanotubes content of the samples. Even better behaviours were observed for the "oxidised purified and lyophilised" SWNTs-1, -2 and -3  
20 samples. The latter improvement may be due to the good dispersion of the SWNTs in the nanocomposites.

### III.D.- Electrical conductivity measurements

#### *Description of the experiments:*

25 [0089] Resistivity was measured using a 4-wire method. The samples are cut into pieces with dimensions 60 mm x 20 mm x 2.8 mm.

[0090] The contacts are made by copper wire (2 mm diameter) and silver paste. The V and I electrodes are  
30 fixed along the plate as: I-V-V-I. The distances between the V-V and V-I electrodes are 35 mm and 12 mm, respectively. A 4-wire microohmmeter (Burnster, Model P 133/0020) was used to measure the resistance between the V

electrodes. Resistivity was calculated using Pouillet's law.

**Results:**

- 5 [0091] The resistivity decreases with increasing concentration of nanotubes in the composite material. With 2.4 wt.% pure MWNTs, the resistivity is higher than  $2 \cdot 10^3 \Omega \cdot \text{cm}$ , but decreases to less than  $10 \Omega \cdot \text{cm}$  with 4.8 wt.% pure MWNTs.
- 10 [0092] Surprisingly, adding 2.4 wt.% of organo-clay to the composite with 2.4 wt.% MWNTs decreases the resistivity from more than  $2 \cdot 10^3 \Omega \cdot \text{cm}$  to about  $8 \cdot 10^1 \Omega \cdot \text{cm}$ . The latter resistivity decrease is achieved due to the homogeneous dispersion of the nanotubes in the polymer
- 15 matrice achieved by the synergetic effect of both organo-clays and carbon nanotubes.
- [0093] Depending on the concentrations and on the mixing procedure, resistivity values between  $8 \Omega \cdot \text{cm}$  and  $8 \cdot 10^{12} \Omega \cdot \text{cm}$  have been found.
- 20 [0094] More generally, it has been shown that the nanocomposites according to the present invention possess an electrical resistivity between  $10^{-4} \Omega \cdot \text{cm}$  and  $8 \cdot 10^{12} \Omega \cdot \text{cm}$ , and preferably between  $1 \Omega \cdot \text{cm}$  and  $10^3 \Omega \cdot \text{cm}$ .

25 **Conclusion**

- [0095] As a conclusion, in the nanocomposites as disclosed in the present invention the components are well dispersed. It has been shown that by adding additives components such as layered silicates nanoparticles, it is
- 30 possible to improve the physical properties of the nanocomposites finally obtained, probably due said homogeneous dispersed structure. Therefore, these nanocomposites provide an industrial breakthrough by

allowing for homogeneous dispersion and increased properties transfer from the carbon nanotubes to the composite materials. Said homogeneous dispersion of the nanotubes in the nanocomposites and the resulting improved  
5 properties transfer to the composites materials are achieved by the synergetic effect of both organo-clays and carbon nanotubes.

[0096] Moreover, the nanocomposites according to the present invention have the advantage of being able to be  
10 produced according to a quite wide range of methods, giving optimal production flexibility.

[0097] Different applications of said nanocomposites could be envisaged taking benefit from their properties. For example, they could be used as flame retardant, as  
15 anti-static material in conductive wires, as wire protector sheath, as anti-cracks in surface protection coatings, as anti-cracks in reinforced materials, as surface protection coatings, as reinforced materials and as or in light-emitting devices.

**Table 2:** Nanotubes dispersion from TEM observations, flame retardant results from TGA and cone calorimeter analysis, and resistivity results of EVA-based nanocomposites.

Sample	EVA (wt.%)	MWNTs (wt.%)		SWNTs-1 (wt.%)		Organo- clay (wt.%)	Nanotubes dispersion (TEM)	TGA Analysis T <sub>max</sub> (°C)	Cone calorimeter analysis			Resistivity (Ω.cm)
		Purif.	Crude	Purif.	Crude				PHRR (kW/m <sup>2</sup> )	Cracks density	Surface quality	
Escorene	100	-	-	-	-	-		477	580			*
1 <sup>a</sup>	97.6	2.4	-	-	-	-	+	501	530	+	+	*
2 <sup>a</sup>	95.2	4.8	-	-	-	-	++	503	400	-	+	8.33
3 <sup>a</sup>	95.2	-	2.4	-	-	2.4	+					
4 <sup>a</sup>	95.2	-	-	-	-	2.4	+					
5 <sup>a</sup>	97.6	-	-	-	-	2.4		511	530	+++	--	*
6 <sup>a</sup>	95.2	-	-	-	-	4.8		505	470	++	-	*
7 <sup>a, b</sup>	95.2	2.4	-	-	-	2.4	+++	503	370	---	+++	83.98
8a <sup>a</sup>	95.2	-	4.8	-	-	-	+++	513	400	--	++	18.24
8b <sup>c</sup>	95.2	-	4.8	-	-	-	+++		400	--	++	128.01
9 <sup>a</sup>	97.6	-	-	2.4	-	-	--		470	+	+	
10 <sup>a</sup>	95.2	-	-	4.8	-	-	-		420	-	+	
11 <sup>a, b</sup>	95.2	-	-	2.4	-	2.4	+		380	---	+++	
12a <sup>a</sup>	95.2	-	-	-	-	-	+					
12b <sup>c</sup>	95.2	-	-	-	-	-	++					

<sup>a</sup> : The screw velocity was 45 rpm and the mixing temperature was 130 °C.

<sup>b</sup> : The nanotubes and nanofiller were premixed before their addition.

<sup>c</sup> : The screw velocity was 120 rpm and the mixing temperature was 140 °C.

\* : The resistivity is too high to be measured.



**Table 3:** Nanotubes dispersion from TEM and Tork observations and flame retardant results from cone calorimeter analysis of PE-based nanocomposites.

Sample	PE <sup>c</sup> (wt.%)	MWNTs (wt.%)		SWNTs-1 (wt.%)		Tork <sup>d</sup> (a.u.)	Nanotubes dispersion (TEM)	Cone calorimeter analysis			
		Purif.	Crude	Purif.	Crude			Time to ignition (s)	PHRR (kW/m <sup>2</sup> )	Cracks density	Surface Quality
PE	100	-	-	-	-			90	454		
13 <sup>a</sup>	95.2	4.8	-	-	-	400	+++	100	289	--	+
14 <sup>a</sup>	90.9	9.1	-	-	-	820	+++	114	359	--	+
15 <sup>a</sup>	95.2	-	4.8	-	-	320	+++	91	326	--	+
16 <sup>a</sup>	90.9	-	9.1	-	-	620	+++	100	374	--	+
17 <sup>a, b</sup>	95.2	-	-	4.8	-	180	++	68	673	++	-
18 <sup>a, b</sup>	90.9	-	-	9.1	-	340	++	63	615	++	-
19 <sup>a</sup>	95.2	-	-	-	4.8	160	++	103	634	++	-
20 <sup>a</sup>	90.9	-	-	-	9.1	240	++	104	476	++	-

<sup>a</sup> : The screw velocity was 45 rpm, the mixing time was 10 min and the mixing temperature was 180 °C.

<sup>b</sup> : The SWNTs were oxidised, purified and lyophilised.

<sup>c</sup> : PE stands for polyethylene BP8063.

<sup>d</sup> : Tork is the relative force needed to mix the nanocomposite. It gives an indication of the relative viscosities of the nanocomposites at the end of the 10 min mixing.

CLAIMS

1. Nanocomposite comprising as components  
5 polymers, carbon nanotubes and layered silicate nanoparticles.

2. Nanocomposite according to claim 1,  
wherein the nanocomposite components are in the form of an  
homogeneous dispersion.

10 3. Nanocomposite according to claim 1 or 2,  
characterised in that the polymers are selected from the  
group consisting of thermoplastic polymers, polyolefins,  
vinyllic polymers, acryl-nitrile polymers, polyacrylates,  
elastomers, fluoro-polymers, thermoplastic polycondensates,  
15 duroplastic polycondensates, silicon resins, thermoplastic  
elastomers, co- and ter-polymers, grafted polymers and  
mixtures thereof.

4. Nanocomposite according to any one of the  
preceding claims, characterised in that the carbon  
20 nanotubes are selected from the group consisting of SWNTs,  
and MWNTs, said carbon nanotubes being pure, partly  
purified, crude or functionalised.

5. Nanocomposite according to any one of the  
preceding claims, characterised in that the layered  
25 silicate nanoparticles are organomodified layered silicate  
nanoparticles.

6. Nanocomposite according to claim 5,  
characterised in that the layered silicate nanoparticles  
are intercalated organo-modified layered silicates from the  
30 chemical class of 2:1 phyllosilicate and smectite.

7. Nanocomposite according to any one of the  
preceding claims, characterised in that the total content  
of the layered silicates and carbon nanotubes varies from

0.01 to 50 wt.%, preferably from 0.5 to 25 wt% , and most preferably between 1 and 10 wt.%.

8. Nanocomposite according to any one of the preceding claims, characterised in that the carbon  
5 nanotubes to the layered silicate nanoparticles weight ratio varies from 0.01 to 100, and preferably between 0.1 and 10.

9. Nanocomposite according to any one of the preceding claims, characterised in that it further  
10 comprises at least one microfiller, preferably in a quantity varying from 1 to 70 wt%.

10. Use of the nanocomposite according to any one of the preceding claims in anti-fire protection structures.

11. Use of the nanocomposite according to any one of the preceding claims as flame retardant.

12. Use of the nanocomposite according to any one of the preceding claims as light-emitter.

13. Use of the nanocomposites according to  
20 any one of the preceding claims as anti-static materials.

14. Use of the nanocomposites according to any one of the preceding claims as conductive wires.

15. Use of the nanocomposites according to any one of the preceding claims as wire protector sheath.

16. Use of the nanocomposites according to  
25 any one of the preceding claims as anti-cracks in surface protection coatings.

17. Use of the nanocomposites according to any one of the preceding claims as anti-cracks in  
30 reinforced materials.

18. Use of the nanocomposites according to any one of the preceding claims as surface protection coatings.

19. Use of the nanocomposites according to any one of the preceding claims as reinforced materials.

20. A process for obtaining the nanocomposite according to any one of the preceding claims, characterised  
5 in that it comprises the step of providing the different components i.e. the polymers, the carbon nanotubes, the layered silicate nanoparticles, and if necessary the microfiller, and the step of mixing said different components in adequate conditions so as to obtain an  
10 homogenous dispersion.

21. The process according to claim 20, characterised in that the step of providing the carbon nanotubes comprises the step of producing said carbon nanotubes on a M/MgO catalyst, wherein M is selected from  
15 the group consisting of Co, Fe, Ni, Mo or their mixtures, and M represents 0.1-50 wt% of the catalyst, the MgO being prepared in situ from metallic magnesium.

22. The process according to claim 20 or 21, wherein the step of providing the carbon nanotubes further  
20 comprises the step of purifying the crude carbon nanotubes as produced in claim 14, by oxidation of the crude nanotubes at 250-500 °C in pure or diluted oxygen for a given time, prior to the dissolution of the spent catalyst, while the nanotubes are well dispersed on it.

23. The process according to any one of claims 20-22, wherein the step of providing the carbon nanotubes further comprises the step of drying the carbon nanotubes produced to obtain a very fine powder, by lyophilisation of a nanotubes/water "wet cake" containing  
30 preferably 80-95 wt% of water.

24. The process according to any one of claims 20-22, wherein the step of providing the carbon nanotubes further comprises the step of drying the carbon nanotubes produced to obtain a very fine powder, by

azeotrope distillation of a nanotubes/water "wet cake" containing preferably 80-95 wt% of water and wherein benzene, toluene or xylene is used to make the azeotrope.

1/1

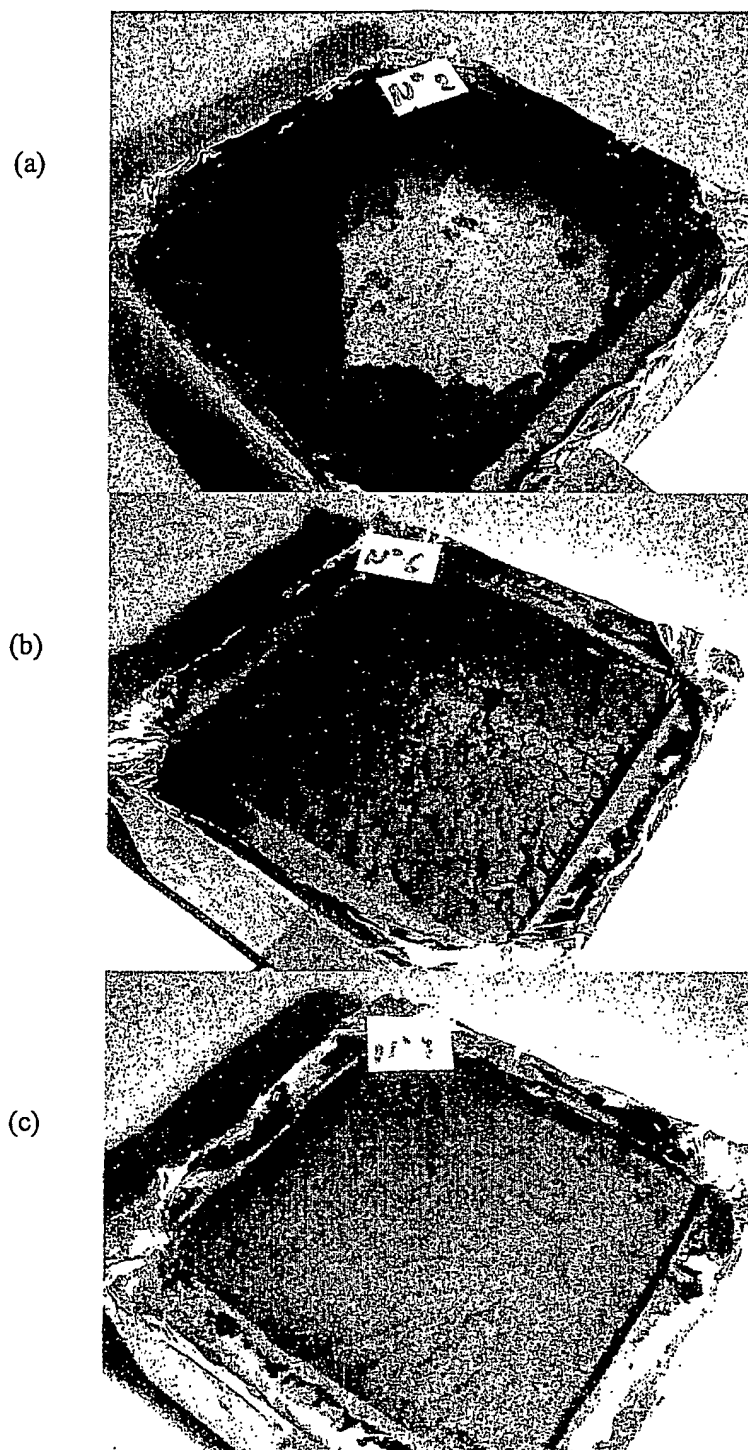


Fig. 1 .

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1, B-4260 CIPLET (BRAIVES) (BE). **ALEXANDRE, Michaël** [BE/BE]; Rue de la Jacinthe, 10, B-4102 OUGREE (BE). **BEYER, Günter** [DE/BE]; Auenweg, 14, B-4700 EUPEN (BE).

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(71) Applicant (*for all designated States except US*): **FACULTES UNIVERSITAIRES NOTRE-DAME DE LA PAIX** [BE/BE]; Rue de Bruxelles 61, B-5000 NAMUR (BE).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **NAGY, Janos, B.** [BE/BE]; Avenue du Bois Carré 5, B-5100 JAMBES (BE). **PIRLOT, Christophe** [BE/BE]; Rue du Brûly, 57, B-5660 PETITE-CHAPELLE (BE). **FONSECA, Antonio** [BE/BE]; Rue Charles de Loupoigne, 15, B-1348 LOUVAIN-LA-NEUVE (BE). **PHILIPPIN, Gregory** [BE/BE]; Rue de la Hêtraie, 7, B-6831 NOIRE-FONTAINE (BE). **DELHALLE, Joseph** [BE/BE]; Rue des Combattants, 19, B-5380 NOVILLE-LES-BOIS (BE). **MEKHALIF, Zineb** [DZ/BE]; Rue Félix Wodon, 29/3, B-5000 NAMUR (BE). **SPORKEN, Robert** [BE/BE]; Place Notre-Dame de la paix, 2 Bte 32, B-5101 ERPENT (BE). **DUBOIS, Philippe** [BE/BE]; Rue Grande,

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(54) Title: NANOCOMPOSITES: PRODUCTS, PROCESS FOR OBTAINING THEM AND USES THEREOF

(57) Abstract: The present invention is related to nanocomposites comprising polymers, carbon nanotubes and layered silicate nanoparticles. The present invention also concerns methods for obtaining said nanocomposites as well as their uses.

# INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

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European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Marucci, A



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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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